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(57) **Abstract**(Modified)
Technical problem The amount of the straw BIRURIN system germicide used is decreased, and the useful plant which reinforces sterilization effect is provided with a validity strengthening agent of a straw BIRURIN system germicide with high safety, and a method for the same.
Means for Solution General formula 1
For drawings please refer to the original document.

(R a hydrogen, low-grade alkyl group, and alkylthio alkyl group, a phenyl group, or a substituted phenyl group) **show and** R^1 A low-grade alkyl group, a cycloalkyl group, benzyl, a substituted benzyl group, A phenethyl group, a phenoxymethyl group, 2-thienyl methyl group, an alkoxy methyl group, or alkyl thiomethyl group. Validity strengthening agent of a straw BIRURIN system germicide containing a cyclohexane derivative or its salt. And an effect enhancement method of applying a validity strengthening agent to a straw BIRURIN system germicide in the range of the validity strengthening agent:straw BIRURIN system germicide weight ratio 1:0.001-1:2.

Claim(s)
Claim 1A general formula **1**
Formula 1

For drawings please refer to the original document.

however, the inside R of a formula -- a hydrogen atom, low-grade alkyl group, and alkylthio alkyl group. A phenyl group or a substituted phenyl group is shown, and R^1 A low-grade alkyl group, A cycloalkyl group, benzyl, a substituted benzyl group, a phenethyl group, a phenoxymethyl group, 2 **CHIE nil methyl group, an alkoxy methyl group, or an alkyl thiomethyl group is shown. Validity strengthening agent of the straw BIRURIN system germicide containing the cyclohexane derivative shown or its salt.
Claim 2 The validity strengthening agent according to claim 1 which is a salt of a cyclohexane derivative.
Claim 3 The validity strengthening agent according to claim 1 or 2 which is calcium salt of a cyclohexane derivative.
Claim 4 An effect enhancement method according to claim 1 to 3, wherein a weight ratio of a validity strengthening agent:straw BIRURIN system germicide applies a validity strengthening agent to a straw BIRURIN system germicide in 1:0.001-1:2.

Detailed Description of the Invention
0001
Field of the Invention This invention relates to a validity strengthening agent of a straw BIRURIN system germicide, and a method for the same.
0002
Description of the Prior Art Although a straw BIRURIN system germicide has an extermination effect in much disease, such as a rice, wheat, greenstuff, and fruit trees, it is a compound out of which a medical harm also tends to come simultaneously. The example the extermination effect is not necessarily enough is reported by a part of **, such as a gray mold disease of greenstuff, sclerotinia rot, and wheat Leptosphaeria nodorum** disease.
0003 On the other hand, the problem over the environmental pollution of agricultural chemicals comes to be taken up, a dropping dose is decreased as much as possible, influence which it has on environment is lessened, and an appearance of the drugs which prevent disease certainly is desired in recent years.
0004
Problem(s) to be Solved by the Invention This invention by reinforcing the effect of enhancement of the effect of a straw BIRURIN system germicide especially the gray mold disease of greenstuff, sclerotinia rot, and wheat Leptosphaeria nodorum, and decreasing the amount of the straw BIRURIN system germicide used, It aims at providing a validity strengthening agent and a method for reinforcing the same of the straw BIRURIN system germicide which has high safety to a useful plant.
0005
Means for Solving the Problem This invention persons are attached to sterilization effect enhancement of a straw BIRURIN system germicide in order to solve these problems, By adding

a cyclohexane derivative which does not have a germicidal action, or its salt as a validity strengthening agent of a straw BIRURIN system germicide, as a result of compounding many compounds, or a compound's coming to hand and inquiring wholeheartedly, With a low dose from which effect sufficient in a straw BIRURIN system germicide independent is not acquired, it found out that a very high bactericidal effect was acquired to much disease, and this invention was completed.

0006A general formula **1** of the following **this invention**

0007

Formula 2

For drawings please refer to the original document.

0008however, the inside R of a formula -- a hydrogen atom, low-grade alkyl group, and alkylthio alkyl group. A phenyl group or a substituted phenyl group is shown, and R^1 A low-grade alkyl group, A cycloalkyl group, benzyl, a substituted benzyl group, a phenethyl group, a phenoxymethyl group, 2 **CHIE nil methyl group, an alkoxy methyl group, or an alkyl thiomethyl group is shown. It is related with a validity strengthening agent and a method for reinforcing the same of the straw BIRURIN system germicide containing the cyclohexane derivative shown or its salt.

0009ODEMANSHIERA grown in the wood which decomposed the straw BIRURIN system germicide in 1969 It goes back to compound Mus Jin (Mucidin) who has sterilization activity out of the culture medium of a MUSHITA bacillus (Oudemansiella mucida) having been discovered. It will be straw BIRURASU in 1978. Same compound straw BIRURIN (Strobilurin) as Mus Jin who has sterilization activity from TENASERASU (Strobilurus tenacellus) was discovered, and this naming turned into a general name after that. Although the mechanism of action checks the energy generation of a bacillus, it differs from conventional respiratory inhibitor, It is specific-action point inhibitor which makes a target the cytochrome b which is a subunit of the complex III of the electron transport system of a mitochondrion, As a structural feature, for example, the compound group which has a 3-methoxy acrylic acid methyl ester group as a substructure, They are general terms, such as a compound group which has a methoxy imino acetic acid methyl ester group as a substructure, or a compound group which has a 2-methoxy imino-N-methyl acetamide group as a substructure.

0010 If attached to a straw BIRURIN system germicide, about an "azoxy straw bottle:new antibacterial-properties extensive spectrum germicide."It was indicated in Society of Synthetic Organic Chemistry, Japan, the 57th volume, No. 4, the 94-98th page, and 1999, and "the mechanism of action of a straw BIRURIN system germicide" is indicated in Pesticide Science Society of Japan, the 24th volume, the 189-196th page, and 1999.

0011 As typical drugs of a straw BIRURIN system germicide, for example An azoxy straw bottle (compound **2**), KURESOKI SIMM methyl (compound **3**), a METOMI nostro bottle (compound **4**), a truffe ROKISHI straw bottle (compound **5**), PIKOKISHISUTOROBIN (compound **6**), etc. can be mentioned.

0012

Formula 3

For drawings please refer to the original document.

0013

Formula 4

For drawings please refer to the original document.

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Formula 5

For drawings please refer to the original document.

0015

Formula 6

For drawings please refer to the original document.

0016
Formula 7

For drawings please refer to the original document.

0017 These compounds are compounds known as a straw BIRURIN system germicide, A compound **2** a compound **3** in the EP patent No. 382,375 gazette The EP patent No. 493,711 gazette, It is the compound in which indicate a compound **4** in the EP patent No. 398,692 gazette, the compound **5** was indicated in the EP patent No. 472,300 gazette, and the compound **6** was indicated in the EP patent No. 278,595 gazette.
0018A cyclohexane derivative used by this invention or a concrete compound of the salt is illustrated from Table 1 to Table 4. The salt of a cyclohexane derivative can take structure of a general formula **9** from a following general formula **7**.
0019 In Table 4 and a general formula **9** from a general formula **7**, R and R^1 express the same meaning as the above from Table 1, M expresses an organic cation or an inorganic cation -- Me -- a methyl group and Et -- in an ethyl group and n-Pr, as for a normal propyl group and c-Pr, a cyclopropyl group and c-Pen express a cyclopentylic group, c-Hex expresses a cyclohexyl group, and Ph expresses a phenyl group.
0020
Formula 8

For drawings please refer to the original document.

0021
Formula 9

For drawings please refer to the original document.

0022
Formula 10

For drawings please refer to the original document.

0023
Table 1

For drawings please refer to the original document.

0024
Table 2

For drawings please refer to the original document.

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Table 3

For drawings please refer to the original document.

0026
Table 4

For drawings please refer to the original document.

0027 It is indicated by JP,58-164543,A, a 59-196840 gazette, 59-231045 gazette, etc. about the cyclohexane derivative.
0028 These cyclohexane derivatives used by this invention or the salt of those does not show a bactericidal effect, when it uses independently, but the bactericidal effect excellent in the straw BIRURIN system germicide is demonstrated by using a cyclohexane derivative or its salt as a sterilization enhancement agent of a straw BIRURIN system germicide.
0029
Embodiment of the Invention The validity strengthening agent of the straw BIRURIN system germicide of this invention, Although it is preferred to use the cyclohexane derivative of this invention or its salt for the pharmaceutical preparation manufacturing process of a straw BIRURIN system germicide, pharmaceutical-preparation-izing it to it in addition, it is also possible to use what pharmaceutical-preparation-ized a cyclohexane derivative or its salt, mixing with straw BIRURIN system sterilization pharmaceutical preparation. In this case, although it may mix at an agrochemical preparation factory or may mix at the time of use of drugs, when it is a granule, it is preferred to add a cyclohexane derivative or its salt at the time of pharmaceutical preparation manufacture of a straw BIRURIN system germicide.
0030 In pharmaceutical-preparation-izing the validity strengthening agent of this invention and mixing with a straw BIRURIN system germicide, it uses it for pharmaceutical preparation, such as powder material, wettable powder, granulation wettable powder, an emulsion, a granule, a fine granule, and suspension pharmaceutical preparation, blending a carrier, a surface-active agent, a dispersing agent, or an adjuvant currently used widely with agrochemical preparation, and carrying out. When mixing a straw BIRURIN system germicide and the validity strengthening agent of this invention, the pharmaceutical preparation or different pharmaceutical preparation of the same pharmaceutical form may be used, and what is necessary is just the combination which a bactericidal effect reinforces.
0031 If the blending ratio of a straw BIRURIN system germicide, a cyclohexane derivative, or its salt is a quantity by which the effect of a straw BIRURIN system germicide is enhanced, can use it, but. Usually, a validity strengthening agent: The range of the weight ratio of a straw BIRURIN system germicide is 1:0.001-1:2, and the range of 1:0.01-1:2 is especially preferred. The quantity of the straw BIRURIN system germicide in pharmaceutical preparation, a cyclohexane derivative, or its salt is 0.1 to 20% (weight), when making it into powder material, a fine granule, and a granule generally, and when making it into an emulsion, wettable powder, and granulation wettable powder, it is 5 to 80% (weight). In the case of suspension pharmaceutical preparation, it is 0.1 to 30% (weight). Of course, even if it is quantity other than this, pharmaceutical-preparation-izing is possible, and it can be used if it is the quantity which demonstrates an effect.
0032
ExampleNext, although the example of pharmaceutical preparation and the example of an examination explain this invention in more detail, the mixing ratio and the adjuvant in pharmaceutical preparation can be changed in the wide range. The following parts show a weight section.
0033 The example 1 (suspension pharmaceutical preparation) of pharmaceutical preparation
Five copies of azoxy straw bottles, ten copies of compounds (A-1), five copies of ammonium chloride, Five copies of condensates (Kao make and trade name:DEMORUN), ten copies of ethylene glycol, 0.1 copy of xanthan gum, and water 64.9 of sodium naphthalenesulfonate It ground, after mixing a part uniformly, and suspension pharmaceutical preparation was obtained.
0034 The example 2 (powder material) of pharmaceutical preparation
The mixed powder agent of five copies of KURESOKI SIMM methyl, five copies of compounds (D-1), five copies of diatomaceous earth, and 85 copies of clay was carried out uniformly, and it was considered as powder material.
0035 The example 3 (wettable powder) of pharmaceutical preparation
The mixed powder agent of three copies of 0.1 copy of azoxy straw bottle, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 89.9 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.

0036 The example 4 (emulsion) of pharmaceutical preparation
Four copies of ten copies of azoxy straw bottle, ten copies of compound (D-1), 20 copies of cyclohexanone, 11 copies of polyoxyethylene-alkyl-aryl-ether, and calcium alkylbenzene sulfonate and 45 copies of methylnaphthalenes were dissolved uniformly, and it was considered as the emulsion.
0037 The example 5 (granule) of pharmaceutical preparation
Preferential grinding of five copies of METOMI nostro bottles, five copies of compounds (A-14), two copies of sodium salt of lauryl alcohol sulfate ester, five copies of sodium ligninsulfonate, two copies of carboxymethyl cellulose, and 81 copies of clay is carried out uniformly. 20% of water was added and kneaded into this mixture, and using the extrusion type granulator, after **14-32 meshes** processing it granular, it dried and was considered as the granule.
0038 The example 6 (wettable powder) of pharmaceutical preparation
The mixed powder agent of three copies of one copy of KURESOKI SIMM methyl, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 89 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.
0039 The example 7 (wettable powder) of pharmaceutical preparation
The mixed powder agent of three copies of 0.01 copy of KURESOKI SIMM methyl, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.
0040 The example 8 (wettable powder) of pharmaceutical preparation
The mixed powder agent of three copies of 0.03 copy of KURESOKI SIMM methyl, five copies of compound (D-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.
0041example 9 (suspension pharmaceutical preparation) of pharmaceutical preparation
It ground, after mixing uniformly ten copies of compounds (A-1), five copies of ammonium chloride, five copies of condensates (Kao make and trade name:DEMORUN) of sodium naphthalenesulfonate, ten copies of ethylene glycol, 0.1 copy of xanthan gum, and 69.9 copies of water, and suspension pharmaceutical preparation was obtained. It is used mixing with a straw BIRURIN system germicide.
0042 The example 10 (wettable powder) of pharmaceutical preparation
The mixed powder agent of three copies of ten copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder. It is used mixing with a straw BIRURIN system germicide.
0043 The example 11 (emulsion) of pharmaceutical preparation
Four copies of 20 copies of compound (D-1), 20 copies of cyclohexanone, 11 copies of polyoxyethylene-alkyl-aryl-ether, and calcium alkylbenzene sulfonate and 45 copies of methylnaphthalenes were dissolved uniformly, and it was considered as the emulsion. It is used mixing with a straw BIRURIN system germicide.
0044 The example 12 (granule) of pharmaceutical preparation
Preferential grinding of ten copies of compounds (D-1), two copies of sodium salt of lauryl alcohol sulfate ester, five copies of sodium ligninsulfonate, two copies of carboxymethyl cellulose, and 81 copies of clay is carried out uniformly. 20 copies of water was added and kneaded into this mixture, and using the extrusion type granulator, after **14-32 meshes** processing it granular, it dried and was considered as the granule. It is used mixing with a straw BIRURIN system germicide.
0045 Next, the example of an examination of this invention is shown.
0046 Example of examination 1 Seeding of every five grains of cucumber seeds (variety: Sagami half-white) was carried out to the plastic pots of each of 9 cm of cucumber gray mold disease preventive effect examination 1 neighborhoods, and it raised in the greenhouse. The wettable powder prepared to the cucumber seedling which the cotyledon developed according to the examples 3 and 6 of pharmaceutical preparation was diluted with water, and 10 ml per one pot was sprinkled. The paper disc was dipped in the spore suspension of gray mold contagion prepared by the yeast glucose liquid medium (0.25% of a yeast extract, glucose 1%) after air-drying, and it put into the cucumber cotyledon surface in a 20 ** moist chamber promptly after planting inoculation. Three days after inoculation, index investigation of the pathopoiesis area ratio of the cotyledon of the whole pot was conducted based on Table 5, by

several one, preventive value was computed and the result was shown in Table 6.

0047

Table 5

For drawings please refer to the original document.

0048

Equation 1

For drawings please refer to the original document.

0049

Table 6

For drawings please refer to the original document.

0050 From the test result, the bactericidal effect of the azoxy straw bottle was reinforced remarkably, and by mixing an azoxy straw bottle (straw BIRURIN system germicide) and pro hexadione calcium salt showed the high cucumber gray mold disease extermination effect clearly surpassed in the iprodione which is a contrast agent.

0051 The cyclohexane derivative shown concretely in the Table 1 - 4 which are used by other this inventions, or its salt showed the effect enhancing effect of the azoxy straw bottle, and showed the high cucumber gray mold disease extermination effect.

0052 Example of examination 2 Seeding of every ten grains of wheat seeds (variety: agriculture and forestry No. 61) was carried out to the plastic pots with a wheat Leptosphaeria nodorum preventive effect examination diameter of 6 cm of each, and it raised in the greenhouse. The wettable powder prepared on the wheat seedling which two leaves developed according to the examples 7 and 8 of pharmaceutical preparation was diluted with water, and was sprinkled 10 ml per one pot. The pycniospore of the wheat Leptosphaeria nodorum bacillus was inoculated after air-drying, and it managed in the greenhouse. Based on Table 7, index investigation of the pathopoiesis area ratio of the first leaf of the whole pot was conducted ten days after inoculation, preventive value was computed by the same method as the example 1 of an examination, and the result was shown in Table 8.

0053

Table 7

For drawings please refer to the original document.

0054

Table 8

For drawings please refer to the original document.

0055 From the test result, the bactericidal effect of the azoxy straw bottle was reinforced remarkably, and by mixing an azoxy straw bottle (straw BIRURIN system germicide) and pro hexadione calcium salt showed the high wheat Leptosphaeria nodorum extermination effect clearly surpassed in the tebuconazole which is a contrast agent.

0056 By adding to an azoxy straw bottle, the cyclohexane derivative concretely shown in Table 4 from Table 1 used by other this inventions or its salt showed the effect enhancing effect of the azoxy straw bottle, and showed the high wheat Leptosphaeria nodorum extermination effect.

0057 Example of examination 3 Seeding of every two grains of apple seeds (variety: ruby) was carried out to the plastic pots with an apple black spot preventive effect examination diameter of 6 cm of each, and it raised in the greenhouse. The foliage leaf diluted with water the wettable powder prepared to the seedling developed four sheets according to the examples 3 and 7 of pharmaceutical preparation, and sprinkled it 10 ml per one pot. The spray inocuration of the spore suspension of an apple black spot bacillus was carried out after air-drying, and 48

time management was promptly carried out in a 20 ** moist chamber. Then, move an apple seedling in a greenhouse, it was made attacked with a disease, index investigation of the pathopoiesis area ratio of top 2 leaves at the time of inoculation was conducted based on Table 7 ten days after inoculation, preventive value was computed by the formula 1, and the result was shown in Table 9.

0058

Table 9

For drawings please refer to the original document.

0059 From the test result, the bactericidal effect of KURESOKI SIMM methyl was reinforced remarkably, and by mixing KURESOKI SIMM methyl (straw BIRURIN system germicide) and pro hexadione calcium salt showed the high apple black spot extermination effect clearly surpassed in Bitertanol which is a contrast agent.

0060 The effect enhancing effect of KURESOKI SIMM methyl was shown, and by adding the cyclohexane derivative concretely shown in Table 4 from Table 1 used by other this inventions or its salt to KURESOKI SIMM methyl showed the high apple black spot extermination effect.

0061

Effect of the Invention The sterilization validity strengthening agent of this invention or its method demonstrates the bactericidal effect outstanding by adding a cyclohexane derivative or its salt to a straw BIRURIN system germicide, and it is a low dose from which effect sufficient in a straw BIRURIN system germicide independent is not acquired, and has a very high bactericidal effect to much disease.

Field of the Invention This invention relates to a validity strengthening agent of a straw BIRURIN system germicide, and a method for the same.

Description of the Prior Art Although a straw BIRURIN system germicide has an extermination effect in much disease, such as a rice, wheat, greenstuff, and fruit trees, it is a compound out of which a medical harm also tends to come simultaneously. The example the extermination effect is not necessarily enough is reported by a part of **, such as a gray mold disease of greenstuff, sclerotinia rot, and wheat Leptosphaeria nodorum** disease.

0003 On the other hand, the problem over the environmental pollution of agricultural chemicals comes to be taken up, a dropping dose is decreased as much as possible, influence which it has on environment is lessened, and an appearance of the drugs which prevent disease certainly is desired in recent years.

Effect of the Invention The sterilization validity strengthening agent of this invention or its method demonstrates the bactericidal effect outstanding by adding a cyclohexane derivative or its salt to a straw BIRURIN system germicide, and it is a low dose from which effect sufficient in a straw BIRURIN system germicide independent is not acquired, and has a very high bactericidal effect to much disease.

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ground, after mixing a part uniformly, and suspension pharmaceutical preparation was obtained.

0034 The example 2 (powder material) of pharmaceutical preparation

The mixed powder agent of five copies of KURESOKI SIMM methyl, five copies of compounds (D-1), five copies of diatomaceous earth, and 85 copies of clay was carried out uniformly, and it was considered as powder material.

0035 The example 3 (wettable powder) of pharmaceutical preparation

The mixed powder agent of three copies of 0.1 copy of azoxy straw bottle, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 89.9 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.

0036 The example 4 (emulsion) of pharmaceutical preparation

Four copies of ten copies of azoxy straw bottle, ten copies of compound (D-1), 20 copies of cyclohexanone, 11 copies of polyoxyethylene-alkyl-aryl-ether, and calcium alkylbenzene sulfonate and 45 copies of methylnaphthalenes were dissolved uniformly, and it was considered as the emulsion.

0037 The example 5 (granule) of pharmaceutical preparation

Preferential grinding of five copies of METOMI nostro bottles, five copies of compounds (A-14), two copies of sodium salt of lauryl alcohol sulfate ester, five copies of sodium ligninsulfonate, two copies of carboxymethyl cellulose, and 81 copies of clay is carried out uniformly. 20% of water was added and kneaded into this mixture, and using the extrusion type granulator, after **14-32 meshes** processing it granular, it dried and was considered as the granule.

0038 The example 6 (wettable powder) of pharmaceutical preparation

The mixed powder agent of three copies of one copy of KURESOKI SIMM methyl, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 89 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.

0039 The example 7 (wettable powder) of pharmaceutical preparation

The mixed powder agent of three copies of 0.01 copy of KURESOKI SIMM methyl, five copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.

0040 The example 8 (wettable powder) of pharmaceutical preparation

The mixed powder agent of three copies of 0.03 copy of KURESOKI SIMM methyl, five copies of compound (D-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder.

0041 The example 9 (suspension pharmaceutical preparation) of pharmaceutical preparation

It ground, after mixing uniformly ten copies of compounds (A-1), five copies of ammonium chloride, five copies of condensates (Kao make and trade name:DEMORUN) of sodium naphthalenesulfonate, ten copies of ethylene glycol, 0.1 copy of xanthan gum, and 69.9 copies of water, and suspension pharmaceutical preparation was obtained. It is used mixing with a straw BIRURIN system germicide.

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The mixed powder agent of three copies of ten copies of compound (A-1), two copies of dinaphthylmethane-disulfonic-acid sodium, and sodium ligninsulfonate and 85 copies of diatomaceous earth was carried out uniformly, and it was considered as wettable powder. It is used mixing with a straw BIRURIN system germicide.

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Four copies of 20 copies of compound (D-1), 20 copies of cyclohexanone, 11 copies of polyoxyethylene-alkyl-aryl-ether, and calcium alkylbenzene sulfonate and 45 copies of methylnaphthalenes were dissolved uniformly, and it was considered as the emulsion. It is used mixing with a straw BIRURIN system germicide.

0044 The example 12 (granule) of pharmaceutical preparation

Preferential grinding of ten copies of compounds (D-1), two copies of sodium salt of lauryl alcohol sulfate ester, five copies of sodium ligninsulfonate, two copies of carboxymethyl cellulose, and 81 copies of clay is carried out uniformly. 20 copies of water was added and kneaded into this mixture, and using the extrusion type granulator, after **14-32 meshes** processing it granular, it dried and was considered as the granule. It is used mixing with a straw BIRURIN system germicide.

0045 Next, the example of an examination of this invention is shown.
0046 Example of examination 1 Seeding of every five grains of cucumber seeds (variety: Sagami half-white) was carried out to the plastic pots of each of 9 cm of cucumber gray mold disease preventive effect examination 1 neighborhoods, and it raised in the greenhouse. The wettable powder prepared to the cucumber seedling which the cotyledon developed according to the examples 3 and 6 of pharmaceutical preparation was diluted with water, and 10 ml per one pot was sprinkled. The paper disc was dipped in the spore suspension of gray mold contagion prepared by the yeast glucose liquid medium (0.25% of a yeast extract, glucose 1%) after air-drying, and it put into the cucumber cotyledon surface in a 20 ** moist chamber promptly after planting inoculation. Three days after inoculation, index investigation of the pathopoiesis area ratio of the cotyledon of the whole pot was conducted based on Table 5, by several one, preventive value was computed and the result was shown in Table 6.
0047
Table 5

For drawings please refer to the original document.

0048
Equation 1

For drawings please refer to the original document.

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Table 6

For drawings please refer to the original document.

0050 From the test result, the bactericidal effect of the azoxy straw bottle was reinforced remarkably, and by mixing an azoxy straw bottle (straw BIRURIN system germicide) and pro hexadione calcium salt showed the high cucumber gray mold disease extermination effect clearly surpassed in the iprodione which is a contrast agent.
0051 The cyclohexane derivative shown concretely in the Table 1 - 4 which are used by other this inventions, or its salt showed the effect enhancing effect of the azoxy straw bottle, and showed the high cucumber gray mold disease extermination effect.
0052 Example of examination 2 Seeding of every ten grains of wheat seeds (variety: agriculture and forestry No. 61) was carried out to the plastic pots with a wheat Leptosphaeria nodorum preventive effect examination diameter of 6 cm of each, and it raised in the greenhouse. The wettable powder prepared on the wheat seedling which two leaves developed according to the examples 7 and 8 of pharmaceutical preparation was diluted with water, and was sprinkled 10 ml per one pot. The pycniospore of the wheat Leptosphaeria nodorum bacillus was inoculated after air-drying, and it managed in the greenhouse. Based on Table 7, index investigation of the pathopoiesis area ratio of the first leaf of the whole pot was conducted ten days after inoculation, preventive value was computed by the same method as the example 1 of an examination, and the result was shown in Table 8.
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hexadione calcium salt showed the high wheat Leptosphaeria nodorum extermination effect clearly surpassed in the tebuconazole which is a contrast agent.
0056 By adding to an azoxy straw bottle, the cyclohexane derivative concretely shown in Table 4 from Table 1 used by other this inventions or its salt showed the effect enhancing effect of the azoxy straw bottle, and showed the high wheat Leptosphaeria nodorum extermination effect.
0057 Example of examination 3 Seeding of every two grains of apple seeds (variety: ruby) was carried out to the plastic pots with an apple black spot preventive effect examination diameter of 6 cm of each, and it raised in the greenhouse. The foliage leaf diluted with water the wettable powder prepared to the seedling developed four sheets according to the examples 3 and 7 of pharmaceutical preparation, and sprinkled it 10 ml per one pot. The spray inocuration of the spore suspension of an apple black spot bacillus was carried out after air-drying, and 48 time management was promptly carried out in a 20 ** moist chamber. Then, move an apple seedling in a greenhouse, it was made attacked with a disease, index investigation of the pathopoiesis area ratio of top 2 leaves at the time of inoculation was conducted based on Table 7 ten days after inoculation, preventive value was computed by the formula 1, and the result was shown in Table 9.
0058
Table 9

For drawings please refer to the original document.

0059 From the test result, the bactericidal effect of KURESOKI SIMM methyl was reinforced remarkably, and by mixing KURESOKI SIMM methyl (straw BIRURIN system germicide) and pro hexadione calcium salt showed the high apple black spot extermination effect clearly surpassed in Bitertanol which is a contrast agent.
0060 The effect enhancing effect of KURESOKI SIMM methyl was shown, and by adding the cyclohexane derivative concretely shown in Table 4 from Table 1 used by other this inventions or its salt to KURESOKI SIMM methyl showed the high apple black spot extermination effect.

Problem(s) to be Solved by the Invention This invention by reinforcing the effect of enhancement of the effect of a straw BIRURIN system germicide especially the gray mold disease of greenstuff, sclerotinia rot, and wheat Leptosphaeria nodorum, and decreasing the amount of the straw BIRURIN system germicide used, It aims at providing a validity strengthening agent and a method for reinforcing the same of the straw BIRURIN system germicide which has high safety to a useful plant.

Means for Solving the Problem This invention persons are attached to sterilization effect enhancement of a straw BIRURIN system germicide in order to solve these problems, By adding a cyclohexane derivative which does not have a germicidal action, or its salt as a validity strengthening agent of a straw BIRURIN system germicide, as a result of compounding many compounds, or a compound's coming to hand and inquiring wholeheartedly, With a low dose from which effect sufficient in a straw BIRURIN system germicide independent is not acquired, it found out that a very high bactericidal effect was acquired to much disease, and this invention was completed.
0006A general formula **1** of the following **this invention**
0007
Formula 2

For drawings please refer to the original document.

0008however, the inside R of a formula -- a hydrogen atom, low-grade alkyl group, and alkylthio alkyl group. A phenyl group or a substituted phenyl group is shown, and R^1 A low-grade alkyl group, A cycloalkyl group, benzyl, a substituted benzyl group, a phenethyl group, a phenoxymethyl group, 2 **CHIE nil methyl group, an alkoxy methyl group, or an alkyl

thiomethyl group is shown. It is related with a validity strengthening agent and a method for reinforcing the same of the straw BIRURIN system germicide containing the cyclohexane derivative shown or its salt.

0009ODEMANSHIERA grown in wood which decomposed a straw BIRURIN system germicide in 1969 It goes back to compound Mus Jin (Mucidin) who has sterilization activity out of culture medium of a MUSHITA bacillus (Oudemansiella mucida) having been discovered. It will be straw BIRURASU in 1978. Same compound straw BIRURIN (Strobilurin) as Mus Jin who has sterilization activity from TENASERASU (Strobilurus tenacellus) was discovered, and this naming turned into a general name after that. Although the mechanism of action checks energy generation of a bacillus, it differs from conventional respiratory inhibitor, It is specific-action point inhibitor which makes a target a cytochrome b which is a subunit of the complex III of an electron transport system of a mitochondrion, As a structural feature, for example, a compound group which has a 3-methoxy acrylic acid methyl ester group as a substructure, They are general terms, such as a compound group which has a methoxy imino acetic acid methyl ester group as a substructure, or a compound group which has a 2-methoxy imino-N-methyl acetamide group as a substructure.

0010 If attached to a straw BIRURIN system germicide, about an "azoxy straw bottle:new antibacterial-properties extensive spectrum germicide."It was indicated in Society of Synthetic Organic Chemistry, Japan, the 57th volume, No. 4, the 94-98th page, and 1999, and "the mechanism of action of a straw BIRURIN system germicide" is indicated in Pesticide Science Society of Japan, the 24th volume, the 189-196th page, and 1999.

0011 As typical drugs of a straw BIRURIN system germicide, for example An azoxy straw bottle (compound **2**), KURESOKI SIMM methyl (compound **3**), a METOMI nostro bottle (compound **4**), a truffe ROKISHI straw bottle (compound **5**), PIKOKISHISUTOROBIN (compound **6**), etc. can be mentioned.

0012
Formula 3

For drawings please refer to the original document.

0013
Formula 4

For drawings please refer to the original document.

0014
Formula 5

For drawings please refer to the original document.

0015
Formula 6

For drawings please refer to the original document.

0016
Formula 7

For drawings please refer to the original document.

0017 These compounds are compounds known as a straw BIRURIN system germicide, A compound **2** a compound **3** in the EP patent No. 382,375 gazette The EP patent No. 493,711 gazette, It is the compound in which indicate a compound **4** in the EP patent No. 398,692 gazette, the compound **5** was indicated in the EP patent No. 472,300 gazette, and the compound **6** was indicated in the EP patent No. 278,595 gazette.

0018 The cyclohexane derivative used by this invention or the concrete compound of the salt is

illustrated from Table 1 to Table 4. The salt of a cyclohexane derivative can take the structure of a general formula **9** from a following general formula **7**.

0019 In Table 4 and a general formula **9** from a general formula **7**, R and R^1 express the same meaning as the above from Table 1, M expresses an organic cation or an inorganic cation -- Me -- a methyl group and Et -- in an ethyl group and n-Pr, as for a normal propyl group and c-Pr, a cyclopropyl group and c-Pen express a cyclopentylic group, c-Hex expresses a cyclohexyl group, and Ph expresses a phenyl group.

0020

Formula 8

For drawings please refer to the original document.

0021

Formula 9

For drawings please refer to the original document.

0022

Formula 10

For drawings please refer to the original document.

0023

Table 1

For drawings please refer to the original document.

0024

Table 2

For drawings please refer to the original document.

0025

Table 3

For drawings please refer to the original document.

0026

Table 4

For drawings please refer to the original document.

0027 It is indicated by JP,58-164543,A, a 59-196840 gazette, 59-231045 gazette, etc. about the cyclohexane derivative.

0028 These cyclohexane derivatives used by this invention or the salt of those does not show a bactericidal effect, when it uses independently, but the bactericidal effect excellent in the straw BIRURIN system germicide is demonstrated by using a cyclohexane derivative or its salt as a sterilization enhancement agent of a straw BIRURIN system germicide.

0029

Embodiment of the Invention The validity strengthening agent of the straw BIRURIN system germicide of this invention, Although it is preferred to use the cyclohexane derivative of this invention or its salt for the pharmaceutical preparation manufacturing process of a straw BIRURIN system germicide, pharmaceutical-preparation-izing it to it in addition, it is also possible to use what pharmaceutical-preparation-ized a cyclohexane derivative or its salt,

mixing with straw BIRURIN system sterilization pharmaceutical preparation. In this case, although it may mix at an agrochemical preparation factory or may mix at the time of use of drugs, when it is a granule, it is preferred to add a cyclohexane derivative or its salt at the time of pharmaceutical preparation manufacture of a straw BIRURIN system germicide.

0030 In pharmaceutical-preparation-izing the validity strengthening agent of this invention and mixing with a straw BIRURIN system germicide, it uses it for pharmaceutical preparation, such as powder material, wettable powder, granulation wettable powder, an emulsion, a granule, a fine granule, and suspension pharmaceutical preparation, blending a carrier, a surface-active agent, a dispersing agent, or an adjuvant currently used widely with agrochemical preparation, and carrying out. When mixing a straw BIRURIN system germicide and the validity strengthening agent of this invention, the pharmaceutical preparation or different pharmaceutical preparation of the same pharmaceutical form may be used, and what is necessary is just the combination which a bactericidal effect reinforces.

0031 If the blending ratio of a straw BIRURIN system germicide, a cyclohexane derivative, or its salt is a quantity by which the effect of a straw BIRURIN system germicide is enhanced, can use it, but. Usually, a validity strengthening agent: The range of the weight ratio of a straw BIRURIN system germicide is 1:0.001-1:2, and the range of 1:0.01-1:2 is especially preferred. The quantity of the straw BIRURIN system germicide in pharmaceutical preparation, a cyclohexane derivative, or its salt is 0.1 to 20% (weight), when making it into powder material, a fine granule, and a granule generally, and when making it into an emulsion, wettable powder, and granulation wettable powder, it is 5 to 80% (weight). In the case of suspension pharmaceutical preparation, it is 0.1 to 30% (weight). Of course, even if it is quantity other than this, pharmaceutical-preparation-izing is possible, and it can be used if it is the quantity which demonstrates an effect.

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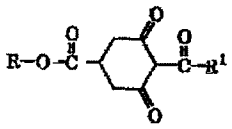
最終頁に続く

(54)【発明の名称】　ストロビルリン系殺菌剤の効力増強剤及びその方法。

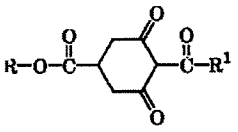
(57)【要約】　（修正有）
【課題】ストロビルリン系殺菌剤の使用量を減少し、殺菌効力を増強させる有用植物に安全性の高いストロビルリン系殺菌剤の効力増強剤及びその方法を提供する。
【解決手段】一般式１



[1]

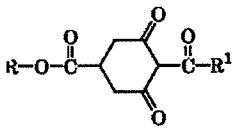
（Ｒは水素、低級アルキル基、アルキルチオアルキル基、フェニル基又は置換フェニル基を示し、R^1は低級アルキル基、シクロアルキル基、ベンジル基、置換ベンジル基、フェネチル基、フェノキシメチル基、２－チエニルメチル基、アルコキシメチル基又はアルキルチオメチル基。）のシクロヘキサン誘導体又はその塩を含有するストロビルリン系殺菌剤の効力増強剤。及びストロビルリン系殺菌剤に効力増強剤を、効力増強剤：ストロビルリン系殺菌剤重量比１：０．００１～１：２の範囲で加える効力増強方法。

【特許請求の範囲】
【請求項１】一般式［１］
【化１】



[1]

（但し、式中Ｒは水素原子、低級アルキル基、アルキルチオアルキル基、フェニル基又は置換フェニル基を示し、Ｒ^{1}は低級アルキル基、シクロアルキル基、ベンジル基、置換ベンジル基、フェネチル基、フェノキシメチル基、２－チエニルメチル基、アルコキシメチル基又はアルキルチオメチル基を示す。）にて示されるシクロヘキサン誘導体又はその塩を含有することを特徴とするストロビルリン系殺菌剤の効力増強剤。
【請求項２】シクロヘキサン誘導体の塩である請求項１記載の効力増強剤。
【請求項３】シクロヘキサン誘導体のカルシウム塩である請求項１又は請求項２記載の効力増強剤。
【請求項４】ストロビルリン系殺菌剤に効力増強剤を、効力増強剤：ストロビルリン系殺菌剤の重量比が１：０．００１～１：２の範囲で加えることを特徴とする請求項１～請求項３記載の効力増強方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、ストロビルリン系殺菌剤の効力増強剤及びその方法に関する。
【０００２】
【従来の技術】ストロビルリン系殺菌剤はイネ、ムギ、野菜類及び果樹類等多くの病害に防除効果を有するが、同時に薬害も出やすい化合物である。又、野菜類の灰色かび病、菌核病及びムギふ枯病等の一部の病害では、その防除効果が必ずしも十分ではない事例が報告されている。
【０００３】一方、近年、農薬の環境汚染に対する問題が取り上げられるようになり、可能な限り投下薬量を減少させ、環境に及ぼす影響を少なくして、確実に病害を防除する薬剤の出現が望まれている。
【０００４】
【発明が解決しようとする課題】本発明はストロビルリン系殺菌剤の効果の増強、特に野菜類の灰色かび病、菌核病及びコムギふ枯病の効果を増強させ、ストロビルリン系殺菌剤の使用量を減少させることにより、有用植物に対して高い安全性を有するストロビルリン系殺菌剤の効力増強剤及びその増強方法を提供することを目的とする。
【０００５】
【課題を解決するための手段】本発明者らは、これらの問題を解決する目的でストロビルリン系殺菌剤の殺菌効力増強につき、多くの化合物を合成し或いは化合物を入手して鋭意研究した結果、殺菌作用を有さないシクロヘキサン誘導体又はその塩をストロビルリン系殺菌剤の効力増強剤として加えることにより、ストロビルリン系殺菌剤単独では十分な効果が得られない低薬量で、多くの病害に対して極めて高い殺菌効果が得られることを見出し、本発明を完成した。
【０００６】本発明は下記の一般式［１］
【０００７】
【化２】



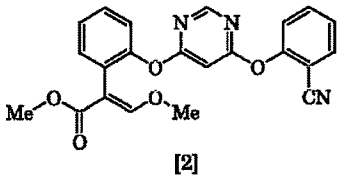
[1]

【０００８】（但し、式中Ｒは水素原子，低級アルキル基、アルキルチオアルキル基、フェニル基又は置換フェニル基を示し、Ｒ^{1}は低級アルキル基、シクロアルキル基、ベンジル基、置換ベンジル基、フェネチル基、フェノキシメチル基、２－チエニルメチル基、アルコキシメチル基又はアルキルチオメチル基を示す。）にて示されるシクロヘキサン誘導体又はその塩を含有するストロビルリン系殺菌剤の効力増強剤及びその増強方法に関するものである。
【０００９】ストロビルリン系殺菌剤は、１９６９年に腐敗した木材に生育しているオーデマンシェラ ムシタ菌（Oudemansiella mucida）の培養液中から殺菌活性を有する化合物ムシジン（Mucidin）が発見されたことに遡る。１９７８年にはストロビルラス テナセラス（Strobilurus tenacellus）から殺菌活性を有するムシジンと同一の化合物ストロビルリン（Strobilurin）が発見され、その後、この命名が一般名となった。作用機構は、菌のエネルギー生産を阻害するが従来の呼吸阻害剤とは異なり、ミトコンドリアの電子伝達系の複合体IIIのサブユニットであるチトクロームｂを標的とする特異作用点阻害剤であり、構造的特徴としては例えば３－メトキシアクリル酸メチルエステル基を部分構造として有する化合物群、メトキシイミノ酢酸メチルエステル基を部分構造として有する化合物群、又は２－メトキシイミノ－Ｎ－メチルアセトアミド基を部分構造として有する化合物群等の総称である。
【００１０】ストロビルリン系殺菌剤については アゾキシストロビン：新規抗菌性広スペクトラム殺菌剤，について、有機合成化学協会誌、第５７巻、第４号、第９４～９８頁、１９９９年に記載され、又、 ストロビルリン系殺菌剤の作用機構，について、日本農薬学会誌、第２４巻、第１８９～１９６頁、１９９９年に記載されている。
【００１１】ストロビルリン系殺菌剤の代表的な薬剤として、例えばアゾキシストロビン（化合物［２］）、ク

レソキシムメチル（化合物［３］）、メトミノストロビン（化合物［４］）、トリフロキシストロビン（化合物［５］）、ピコキシストロビン（化合物［６］）等を挙げることができる。

【００１２】

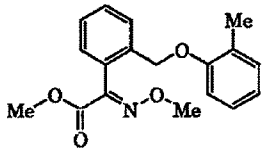
【化３】



[2]

【００１３】

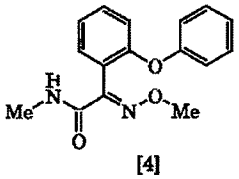
【化４】



[3]

【００１４】

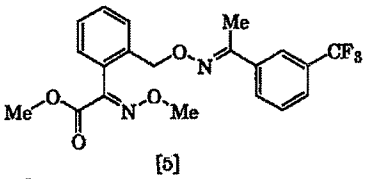
【化５】



[4]

【００１５】

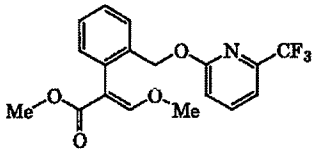
【化６】



[5]

【００１６】

【化７】



[6]

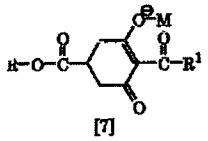
【００１７】これらの化合物はストロビルリン系殺菌剤として知られた化合物であり、化合物［２］はＥＰ特許第３８２，３７５号公報に、化合物［３］はＥＰ特許第４９３，７１１号公報、化合物［４］はＥＰ特許第３９８，６９２号公報、化合物［５］はＥＰ特許第４７２，３００号公報、化合物［６］はＥＰ特許第２７８，５９５号公報に記載された化合物である。

【００１８】本発明で使用するシクロヘキサン誘導体又はその塩の具体的な化合物を表１から表４に例示する。尚、シクロヘキサン誘導体の塩は下記一般式［７］から一般式［９］の構造をとり得る。

【００１９】又、表１から表４及び一般式［７］から一般式［９］において、Ｒ及びR^1は前記と同じ意味を表し、Ｍは有機カチオン又は無機カチオンを表し、Ｍｅはメチル基、Ｅｔはエチル基、ｎ－Ｐｒはノルマルプロピル基、ｃ－Ｐｒはシクロプロピル基、ｃ－Ｐｅｎはシクロペンチル基、ｃ－Ｈｅｘはシクロヘキシル基、Ｐｈはフェニル基を表す。

【００２０】

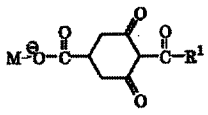
【化８】



[7]

【００２１】

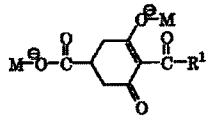
【化９】



[8]

【００２２】

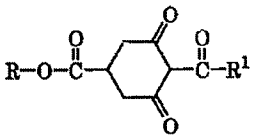
【化１０】

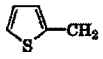
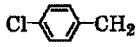
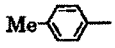


[9]

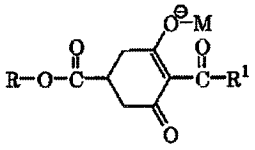
【００２３】

【表1】



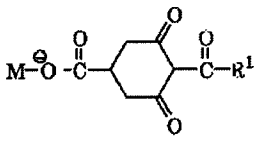
化合物番号	R	R^1
A-1	Et	Et
A-2	Et	c-Pr
A-3	Et	c-Pen
A-4	Me	c-Hex
A-5	Et	$PhCH_2$
A-6	Et	$PhCH_2CH_2$
A-7	Et	$PhOCH_2$
A-8	Et	$EtOCH_2$
A-9	Et	$EtSCH_2$
A-10	Et	
A-11	$MeSCH_2CH_2$	n-Pr
A-12	Et	
A-13	Ph	n-Pr
A-14		n-Pr

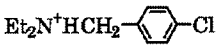
【0024】 【表2】



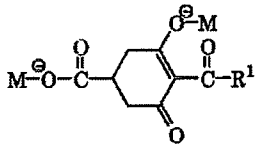
化合物番号	R	R^1	M
B-1	Me	Me	$H_2N^+(CH_2CH_2OH)_2$
B-2	Et	Me	$H_2N^+Et_2$
B-3	Et	Et	$H_2N^+(CH_2CH_2OH)_2$

【0025】 【表3】



化合物番号	R^1	M
C-1	n-Pr	HN^+Et_3
C-2	Et	
C-3	Et	Na^+

【0026】 【表4】



化合物番号	R^1	M
D-1	Et	1/2 Ca^{++}
D-2	Et	Na^+
D-3	Et	$H_2N^+(CH_2CH_2OH)_2$

【００２７】シクロヘキサン誘導体については特開昭５８－１６４５４３号公報、同５９－１９６８４０号公報、同５９－２３１０４５号公報等に開示されている。

【００２８】本発明で使用するこれらのシクロヘキサン誘導体又はその塩は単独で用いた場合には殺菌効果を示さないが、シクロヘキサン誘導体又はその塩をストロビルリン系殺菌剤の殺菌増強剤として使用することにより、ストロビルリン系殺菌剤が優れた殺菌効果を発揮する。

【００２９】

【発明の実施形態】本発明のストロビルリン系殺菌剤の効力増強剤は、本発明のシクロヘキサン誘導体又はその塩をストロビルリン系殺菌剤の製剤製造過程において加え、製剤化して使用するのが好ましいが、シクロヘキサン誘導体又はその塩を製剤化したものをストロビルリン系殺菌製剤と混合して使用することも可能である。この場合、農薬製剤工場で混合するか、或いは薬剤の使用時に混合しても良いが，粒剤の場合には、ストロビルリン系殺菌剤の製剤製造時にシクロヘキサン誘導体又はその塩を加えることが好ましい。

【００３０】本発明の効力増強剤を製剤化して、ストロビルリン系殺菌剤と混合する場合には、農薬製剤で汎用されている担体、界面活性剤、分散剤又は補助剤等を配合して、粉剤、水和剤、顆粒水和剤、乳剤、粒剤、微粒剤、懸濁製剤等の製剤にして使用する。ストロビルリン系殺菌剤と本発明の効力増強剤を混合する場合には、同じ剤型の製剤或いは異なる製剤で良く、殺菌効果が増強する組み合わせであれば良い。

【００３１】ストロビルリン系殺菌剤とシクロヘキサン誘導体又はその塩の配合割合はストロビルリン系殺菌剤の効果が増強される量であれば使用することができるが、通常、効力増強剤：ストロビルリン系殺菌剤の重量比が１：０．００１～１：２の範囲であり、特に１：０．０１～１：２の範囲が好ましい。製剤中におけるストロビルリン系殺菌剤とシクロヘキサン誘導体又はその塩の量は、一般的に粉剤、微粒剤及び粒剤とする場合は０．１～２０％（重量）であり、乳剤、水和剤及び顆粒水和剤とする場合は５～８０％（重量）である。又、懸濁製剤の場合には０．１～３０％（重量）である。もちろん、これ以外の量であっても製剤化可能であり、効果を発揮させる量であれば使用することができる。

【００３２】

【実施例】次に、本発明を製剤例及び試験例でより詳しく説明するが、製剤中の混合割合及び補助剤は広い範囲で変更することができる。尚、以下の部は重量部を示す。

【００３３】製剤例１（懸濁製剤）

アゾキシストロビン５部、化合物（Ａ－１）１０部、塩化アンモニウム５部、ナフタレンスルホン酸ナトリウムの縮合物（花王製、商品名：デモールＮ）５部、エチレングリコール１０部、キサンタンガム０．１部及び水６４．９　部を均一に混合した後粉砕し懸濁製剤を得た。

【００３４】製剤例２（粉剤）

クレソキシムメチル５部、化合物（Ｄ－１）５部、珪藻土５部及びクレー８５部を均一に混合粉剤して粉剤とした。

【００３５】製剤例３（水和剤）

アゾキシストロビン０．１部、化合物（Ａ－１）５部、ジナフチルメタンジスルホン酸ナトリウム２部、リグニンスルホン酸ナトリウム３部及び珪藻土８９．９部を均一に混合粉剤して水和剤とした。

【００３６】製剤例４（乳剤）

アゾキシストロビン１０部、化合物（Ｄ－１）１０部、シクロヘキサノン２０部、ポリオキシエチレンアルキルアリールエーテル１１部、アルキルベンゼンスルホン酸カルシウム４部及びメチルナフタレン４５部を均一に溶解して乳剤とした。

【００３７】製剤例５（粒剤）

メトミノストロビン５部、化合物（Ａ－１４）５部、ラウリルアルコール硫酸エステルのナトリウム塩２部、リグニンスルホン酸ナトリウム５部、カルボキシメチルセルロース２部及びクレー８１部を均一に混合粉砕する。この混合物に水２０％を加えて練合し、押出式造粒機を用いて１４～３２メッシュの粒状に加工したのち、乾燥して粒剤とした。

【００３８】製剤例６（水和剤）

クレソキシムメチル1部、化合物（A－1）5部、ジナフチルメタンジスルホン酸ナトリウム2部、リグニンスルホン酸ナトリウム3部及び珪藻土89部を均一に混合粉剤して水和剤とした。

【0039】製剤例7（水和剤）

クレソキシムメチル0．01部、化合物（A－1）5部、ジナフチルメタンジスルホン酸ナトリウム2部、リグニンスルホン酸ナトリウム3部及び珪藻土85部を均一に混合粉剤して水和剤とした。

【0040】製剤例8（水和剤）

クレソキシムメチル0．03部、化合物（D－1）5部、ジナフチルメタンジスルホン酸ナトリウム2部、リグニンスルホン酸ナトリウム3部及び珪藻土85部を均一に混合粉剤して水和剤とした。

【0041】製剤例9（懸濁製剤）

化合物（A－1）10部、塩化アンモニウム5部、ナフタレンスルホン酸ナトリウムの縮合物（花王製、商品名：デモールN）5部、エチレングリコール10部、キサンタンガム0．1部、水69．9部を均一に混合した後粉砕し、懸濁製剤を得た。ストロビルリン系殺菌剤と混合して使用する。

【0042】製剤例10（水和剤）

化合物（A－1）10部、ジナフチルメタンジスルホン酸ナトリウム2部、リグニンスルホン酸ナトリウム3部及び珪藻土85部を均一に混合粉剤して水和剤とした。ストロビルリン系殺菌剤と混合して使用する。

【0043】製剤例11（乳剤）

化合物（D－1）20部、シクロヘキサノン20部、ポリオキシエチレンアルキルアリールエーテル11部、アルキルベンゼンスルホン酸カルシウム4部及びメチルナフタレン45部を均一に溶解して乳剤とした。ストロビルリン系殺菌剤と混合して使用する。

【0044】製剤例12（粒剤）

化合物（D－1）10部、ラウリルアルコール硫酸エステルのナトリウム塩2部、リグニンスルホン酸ナトリウム5部、カルボキシメチルセルロース2部及びクレー81部を均一に混合粉砕する。この混合物に水20部を加えて練合し、押出式造粒機を用いて14～32メッシュの粒状に加工したのち、乾燥して粒剤とした。ストロビルリン系殺菌剤と混合して使用する。

【0045】次に本発明の試験例を示す。

【0046】試験例1　キュウリ灰色かび病予防効果試験

一辺9cmのプラスチックポット各々に、キュウリ種子（品種：相模半白）を5粒づつ播種し、温室内で育成した。子葉が展開したキュウリ幼苗に、製剤例3及び6に準じて調製した水和剤を水で希釈し、1ポット当たり10mlを散布した。風乾後、イーストグルコース液体培地（酵母エキス0．25%、グルコース1%）で調製した灰色かび病菌の胞子懸濁液にペーパーディスクを浸し、キュウリ子葉表面に置床接種後、直ちに20℃湿室内に入れた。接種3日後に、ポット全体の子葉の発病面積割合を表5に基づき指数調査し、数1によって防除価を算出し、その結果を表6に示した。

【0047】

【表5】

指数	調査基準
n0	健全葉数
n1	発病面積が無処理区の5%未満の葉数
n2	発病面積が無処理区の5%以上33.3%未満の葉数
n3	発病面積が無処理区の33.3%以上66.6%未満の葉数
n4	発病面積が無処理区の66.6%以上の葉数

【0048】

【数1】

$$\text{防除価(\%)} = \left(1 - \frac{(n1\times1)+(n2\times2)+(n3\times3)+(n4\times4)}{\text{全調査葉数}\times4}\right)\times100$$

【0049】

【表6】

供試化合物	濃度(ppm)	防除価(%)
アゾキシストロビン+化合物A-1 (本発明)	1+50	58.6
アゾキシストロビン+化合物A-1 (本発明)	10+50	100.0
アゾキシストロビン (比較)	1	6.2
アゾキシストロビン (比較)	10	53.4
化合物A-1 (比較)	50	0.0
イプロジオン (対照)	1	3.3
イプロジオン (対照)	10	51.7

【0050】試験結果から、アゾキシストロビン（ストロビルリン系殺菌剤）とプロヘキサジオンカルシウム塩とを混合することにより、アゾキシストロビンの殺菌効果を著しく増強させ、対照剤であるイプロジオンに明らかに優る高いキュウリ灰色かび病防除効果を示した。

【0051】尚，その他の本発明で使用する表1～表4で具体的に示したシクロヘキサン誘導体又はその塩は、アゾキシストロビンの効力増強効果を示し、高いキュウリ灰色かび病防除効果を示した。

【0052】試験例2　ムギふ枯病予防効果試験

直径6cmのプラスチックポット各々に、コムギ種子（品種：農林61号）を10粒づつ播種し、温室内で育成した。2葉が展開したコムギ苗に、製剤例7及び8に準じて調製した水和剤を水で希釈し、1ポット当たり10ml散布した。風乾後、コムギふ枯病菌の柄胞子を接種し、温室内で管理した。接種10日後にポット全体の第1葉の発病面積割合を表7に基づき指数調査し、試験例1と同様の方法により防除価を算出し、その結果を表8に示した。

【0053】

【表7】

指数	調査基準
n0	健全葉数
n1	発病面積が無処理区の5%未満の葉数
n2	発病面積が無処理区の5%以上25%未満の葉数
n3	発病面積が無処理区の25%以上50%未満の葉数
n4	発病面積が無処理区の50%以上の葉数

【0054】

【表8】

供試化合物	濃度(ppm)	防除価(%)
アゾキシストロビン+化合物D-1 (本発明)	0.1+50	100.0
アゾキシストロビン+化合物D-1 (本発明)	0.3+50	100.0
アゾキシストロビン (比較)	0.1	29.6
アゾキシストロビン (比較)	0.3	53.1
化合物D-1 (比較)	50	0.0
テブコナゾール (対照)	0.1	0.0
テブコナゾール (対照)	0.3	14.3

【0055】試験結果から、アゾキシストロビン（ストロビルリン系殺菌剤）とプロヘキサジオンカルシウム塩とを混合することにより、アゾキシストロビンの殺菌効果を著しく増強させ、対照剤であるテブコナゾールに明らかに優る高いムギふ枯病防除効果を示した。

【0056】尚、その他の本発明で使用する表1から表4で具体的に示したシクロヘキサン誘導体又はその塩はアゾキシストロビンに加えることにより、アゾキシストロビンの効力増強効果を示し、高いムギふ枯病防除効果を示した。

【0057】試験例3　リンゴ黒星病予防効果試験

直径6cmのプラスチックポット各々に、リンゴ種子

（品種：紅玉）を２粒づつ播種し、温室内で育成した。本葉が４枚展開した実生苗に、製剤例３及び７に準じて調製した水和剤を水で希釈し、１ポット当たり１０ｍｌ散布した。風乾後、リンゴ黒星病菌の胞子懸濁液を噴霧接種し、直ちに２０℃の湿室内で48時間管理した。その後、リンゴ苗を温室内に移し発病させ、接種１０日後に接種時の上位２葉の発病面積割合を表７に基づき指数調査し、式１により防除価を算出し、その結果を表９に示した。

【００５８】

【表９】

供試化合物	濃度(ppm)	防除価(%)
クレソキシムメチル＋化合物Ｄ－１　（本発明）	0.1＋50	67.3
クレソキシムメチル＋化合物Ｄ－１　（本発明）	1.0＋50	100.0
クレソキシムメチル（比較）	0.1	35.7
クレソキシムメチル（比較）	1.0	81.0
化合物Ｄ－１（比較）	50.0	0.0
ビテルタノール（対照）	0.1	10.4
ビテルタノール（対照）	1.0	75.0

【００５９】試験結果から、クレソキシムメチル（ストロビルリン系殺菌剤）とプロヘキサジオンカルシウム塩とを混合することにより、クレソキシムメチルの殺菌効果を著しく増強させ、対照剤であるビテルタノールに明らかに優る高いリンゴ黒星病防除効果を示した。

【００６０】尚、その他の本発明で使用する表１から表４で具体的に示したシクロヘキサン誘導体又はその塩をクレソキシムメチルに加えることにより、クレソキシムメチルの効力増強効果を示し、高いリンゴ黒星病防除効果を示した。

【００６１】

【発明の効果】本発明の殺菌効力増強剤又はその方法はストロビルリン系殺菌剤にシクロヘキサン誘導体又はその塩を加えることにより、優れた殺菌効果を発揮し、ストロビルリン系殺菌剤単独では十分な効果が得られない低薬量で、多くの病害に対して極めて高い殺菌効果を有する。

フロントページの続き

Ｆターム(参考)　4H011 AA01 BA01 BA02 BB06 BB09
BC01 BC03 BC05 BC06 BC07
BC08 BC18 BC19 BC20 DA02
DA13 DA15 DC03 DC04 DC05
DC06 DC08 DD03 DH02 DH03
DH10 DH14